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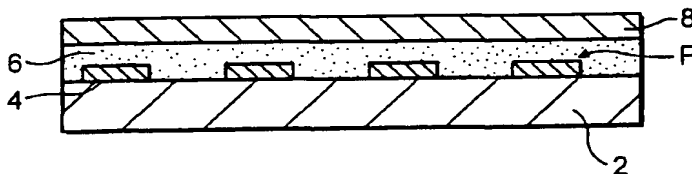
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(54) Title: A FORMULATION FOR DEPOSITING A CONJUGATED POLYMER LAYER



polymer layer on a substrate by an ink-jet method.

(57) Abstract: A formulation for depositing a polymer layer in the production of a light-emission device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a dialkyl- or trialkyl-substituted aromatic hydrocarbon, at least two of the alkyl substituents being ortho to one another; and the use of such formulation in the deposition of a

A FORMULATION FOR DEPOSITING A CONJUGATED POLYMER LAYER

The present invention relates to a formulation for depositing a conjugated polymer layer in a light-emissive device (LED).

Light-emissive devices using as the light-emissive layer a semiconductive conjugated polymer are known. Figure 1 shows the construction of a simple light-emissive device. A glass or plastics substrate 2 is coated with an anode layer 4, for example in the form of indium tin oxide. The anode can be patterned in the form of elongate strips. The anode layer may be coated with a hole transport layer. A light-emissive polymer layer 6 is then deposited followed by the deposition of an electron transport layer. The device structure is then completed by the deposition of a cathode layer 8. By way of example, the cathode layer can be calcium or aluminium. The cathode layer 8 can be patterned in crosswise strips to define pixels P where the anode and cathode overlap. Alternatively with an unpatterned cathode, light emissive strips can be defined. Further alternatively, the pixels may be defined on an active matrix back-plane and the cathode may be patterned or unpatterned. When an electric field is applied between the anode and cathode, holes and electrons are injected into the light-emissive polymer layer 6. The holes and electrons recombine in the polymer layer and a proportion decay radiatively to generate light.

The hole transport layer can be comprised generally of any compound capable of sustaining hole transport. Examples of suitable materials are organic conductors such as the following conducting polymers: polyaniline, polyethylenedioxythiophene and other polythiophenes, polypyrrole, etc. in their doped forms. Other alternative

materials are conjugated polyamines and also low molecular weight amines such as TPD.

The light-emissive layer may comprise any molecular or polymeric compounds which are capable of sustaining charge carrier transport and also capable of light emission under device driving conditions. Examples include fluorescent organic compounds and conjugated polymers such as Alq3, polyphenylenes and derivatives, polyfluorenes and derivatives, polythiophenes and derivatives, polyphenylene vinylenes and derivatives, polymers containing hetero-aromatic rings, etc..

The electron transport layer may generally comprise any material capable of sustaining electron transport. Examples include perylene systems, Alq3, polyfluorenes or polyfluorene copolymers, polymers containing heteroaromatic rings, etc..

The device may contain any combination of the above layers provided it includes at least one light-emissive layer.

OLEDs are described in US Patent No. 5,247,190 or in US Patent No. 4,539,507, the contents of which are incorporated herein by reference. In US 5,247,190 the active organic layer is a light-emissive semiconductive conjugated polymer and in US 4,539,507 the active organic layer is a light-emissive sublimed molecular film.

Conventionally, the polymer layer was typically deposited by spin-coating or metered blade-coating a polymer solution onto the anode and then either allowing the solvent to evaporate at RTP, or driving off the solvent using heat treatment and/or reduced pressure. The polymer was the light-emissive polymer itself cast directly from solution, or a precursor to the polymer, which is converted to the

light-emissive polymer during a heat treatment step. The polymer layer can comprise a blend of two or more materials, such as a blend of two or more polymers.

The polymer layer(s) may also be deposited by supplying a solution-processible material including the polymer through a plurality of elongate bores, either through the effect of gravity or under pressure or utilising the effect of surface tension. This facilitates direct deposition or patterning of the polymer films as required.

Deposition of the polymer layer(s) by means of an ink-jet method is a particularly preferred technique. The ink-jet method is described, for example, in EP0880303A1, the content of which is incorporated herein by reference.

It is desirable to use material formulations with which thin polymer films exhibiting excellent emission uniformity can be produced.

The present applicant's own previous application PCT/GB00/03349 discloses examples of formulations for depositing conjugated polymers based on polyalkylated benzenes such as cymene and isodurene.

It is also an aim of the present invention to provide formulations that facilitate the direct deposition of patterned polymer films. In particular, it is an aim of the present invention to provide a formulation with which conjugated polymer films that exhibit improved emission uniformity can be deposited.

According to a first aspect of the present invention, there is provided a formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the

solvent including a dialkyl- or trialkyl- substituted aromatic hydrocarbon, at least two of the alkyl substituents being ortho to one another.

The solvent preferably includes one or more of 1,2-dimethyl benzene, 1,2,3-trialkylbenzene and 1,2,4-trialkylbenzene. 1,2-dimethyl benzene and 1,2,3-trialkylbenzene are particularly preferred.

According to a second aspect of the present invention, there is provided a formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a trialkylbenzene.

According to a third aspect of the present invention there is provided a method of depositing a polymer layer by supplying a solution processible formulation according to the first or second aspects of the present invention via a plurality of elongate bores onto a substrate.

According to a fourth aspect of the present invention, there is provided a method of forming a polymer layer on a substrate comprising the step of depositing a formulation according to the first or second aspects of the present invention on a substrate by an ink-jet method.

For the purposes of this application, the term "polymer" includes homopolymers and copolymers, and also includes layers of polymer blends as well as layers of single polymers; and the term "polymer layer" includes a layer of relatively small dimensions, such as a layer having dimensions corresponding to a single pixel in a pixelated display, as well as layers of larger dimensions.

For the purposes of this application, the term "alkyl" refers to linear or branched alkyl substituents having up to 6 carbon atoms.

The resulting formulation preferably has a surface tension in the range of 25 to 40mN/m at 20°C, a viscosity of 2 to 8cPs at 20°C, and a w/v polymer concentration of 0.25 to 1.5%, preferably 0.5 to 1%. A formulation having such properties is particularly suited for deposition by ink-jet printing. The formulation should also have a contact angle appropriate for the substrate on which the deposition is carried out. For example, in the case of a polyimide substrate, the contact angle should be in the range of 30 to 60 degrees.

The formulation may include one or more additional types of solvents provided that the resulting formulation has the necessary fluid properties for the particular deposition technique. The presence of even a relatively small proportion of, for example, one or more trialkyl benzenes in the formulation can serve to improve the stability of the formulation and/or the fluid properties of the formulation.

For the purposes of this application, the term conjugated polymer refers to polymers, including oligomers such as dimers, trimers etc., which are fully conjugated (i.e. are conjugated along the entire length of the polymer chain) or are partially conjugated (i.e. which include non-conjugated segments in addition to conjugated segments).

The polymer may have an average molecular weight in the range of 10,000 to 500,000, more particularly in the range of 10,000 to 300,000.

The polymer may be a polymer suitable for use in a light-emissive layer, a hole transport layer or an electron transport layer in an organic light-emissive device.

In a preferred example, the conjugated polymer can be a light-emissive polymer, hole transport polymer or electron transport polymer itself, or a precursor to a light-emissive polymer, hole transport polymer or electron transport polymer. The conjugated polymer or its precursor can be any suitable polymer, and in particular can be any one of the following:

a) conducting polymers such as polyaniline (PANI) and derivatives, polythiophenes and derivatives, polypyrrole and derivatives, polyethylene dioxythiophene; doped forms of all these and particularly polystyrene sulphonic acid-doped polyethylene dioxythiophene (PEDT/PSS);

b) solution processible charge transporting and/or luminescent/electro-luminescent polymers, preferably conjugated polymers such as: polyphenylenes and derivatives, polyphenylene vinylenes and derivatives, polyfluorenes and derivatives, tri-aryl containing polymers and derivatives, precursor polymers in various forms, copolymers (including the above-named polymer classes), generally random and block copolymers, polymers with the active (charge transporting and/or luminescent) species attached as side-groups to the main chain, thiophenes and derivatives, etc..

It is also envisaged that the present invention is also applicable to formulations comprising other compounds such as solution processible molecular compounds including spiro-compounds, such as described for example in EP-A-

0676461; and other inorganic compounds, e.g. solution-processible organometallic precursor compounds to fabricate insulators or conductors.

The conjugated polymer may, for example, comprise a fluorene-based polymer, or a copolymer containing fluorene units with other units such as triarylamine units or benzylthiadiazole (BT) units, or a blend of two or more of such polymers.

For a better understanding of the invention and to show how the same may be carried into effect, embodiments of the present invention are described hereunder, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a diagram of a light-emissive device;
Figure 2 is a diagram illustrating a method of depositing various polymer layers; and
Figure 3 shows the structure of recurring units and polymers used in the examples.

Figure 2 illustrates a deposition technique for depositing a polymer layer 6 onto the patterned anode 4. A plurality of elongate bores 10 are illustrated, each aligned with a respective trough 8. The elongate bores 10 are connected via a conduit 12 to a reservoir 14 holding the solution to be deposited. The solution is supplied through the elongate bores 10 under pressure or by gravity to deposit the light emitting polymer layer 6.

Specific formulations according to the present invention are discussed herebelow.

Example 1

The first exemplified formulation is 1% w/v of a triblend containing approximately 14 wt.% of a ternary polymer containing fluorene (F8) units (shown in Figure 3a), benzylthiadiazole (BT) units (shown in Figure 3b) and triarylene units shown in Figure 3c, 56 wt.% of F8BT (shown in Figure 3d) and 30wt.% TFB (shown in Figure 3e) in 1,2,4-trimethylbenzene. The resulting formulation had a viscosity of 3.8cps at 20°C and a surface tension of 28mN/m at 20°C.

Example 2

According to the second example, the formulation comprises 1% w/v of the triblend referred to in Example 1 in a solvent mixture containing 20vol.% 1,2,4-trimethylbenzene and 80vol.% xylene. The formulation had a solution viscosity of 2.9cps at 20°C and a surface tension of 28mN/m at 20°C.

A sample of the formulation was deposited on a substrate and was vacuum dried. The PL efficiency of the thus produced polymer layer was found to be 43%. Drying a layer of the same formulation at 80°C for 13.5 hours resulted in a polymer layer having a PL efficiency of 39%.

Example 3

According to a third example, the formulation comprises 1% w/v of the triblend referred to in Example 1 in a solvent mixture containing 50vol.% 1,2,4-trimethylbenzene and 50vol.% xylene. The formulation had a solution viscosity of 2.82cps at 20°C and a surface tension of 28mN/m at 20°C.

The addition of the trimethyl benzene is found to significantly increase the stability of the formulation.

1,2-dimethyl benzene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene were also found to be good solvents for a fluorene-thiophene polymer having an average molecular weight of about 266,000.

CLAIMS:

1. A formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a dialkyl- or trialkyl- substituted aromatic hydrocarbon, at least two of the alkyl substituents being ortho to one another.
2. A formulation according to claim 1 wherein the solvent includes a dialkyl- or trialkyl-substituted benzene, at least two of the alkyl substituents being ortho to one another.
3. A formulation according to claim 1 or claim 2 wherein each alkyl substituent is independently a C1-C6 alkyl group.
4. A formulation according to claim 3 wherein each alkyl substituent is a methyl group.
5. A formulation according to claim 4 wherein the solvent includes 1,2-dimethylbenzene.
6. A formulation according to claim 4 wherein the solvent includes 1,2,3-trimethylbenzene.
7. A formulation for depositing a polymer layer in the production of a light-emissive device, the formulation including a conjugated polymer dissolved in a solvent, the solvent including a trialkylbenzene.

8. A formulation according to claim 7 wherein the solvent also includes xylene.
9. A formulation according to claim 8 wherein the solvent comprises 20% to 100% by weight of a trialkylbenzene and up to 80% by weight of xylene..
10. A formulation according to any preceding claim wherein the conjugated polymer is a light-emissive polymer.
11. A formulation according to any preceding claim wherein the polymer includes a fluorene-based polymer.
12. A formulation according to any preceding claim wherein the polymer includes a polymer containing fluorene and triarylamine units.
13. A formulation according to any preceding claim wherein the polymer comprises a blend of a fluorene-based polymer and a polymer containing fluorene and triarylamine units.
14. A method of depositing a polymer layer by supplying a solution processible formulation according to any preceding claim via a plurality of elongate bores onto a substrate.
15. A method of forming a polymer layer on a substrate comprising the step of depositing a formulation according to any preceding claim on a substrate by ink-jet printing.

16. The use of a formulation according to any preceding claim in an ink-jet method of depositing a polymer layer.

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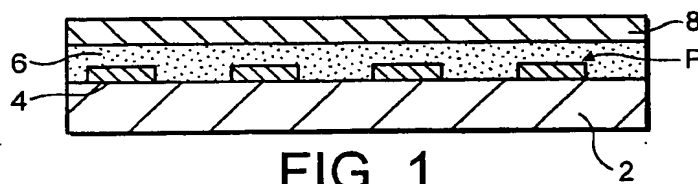


FIG. 1

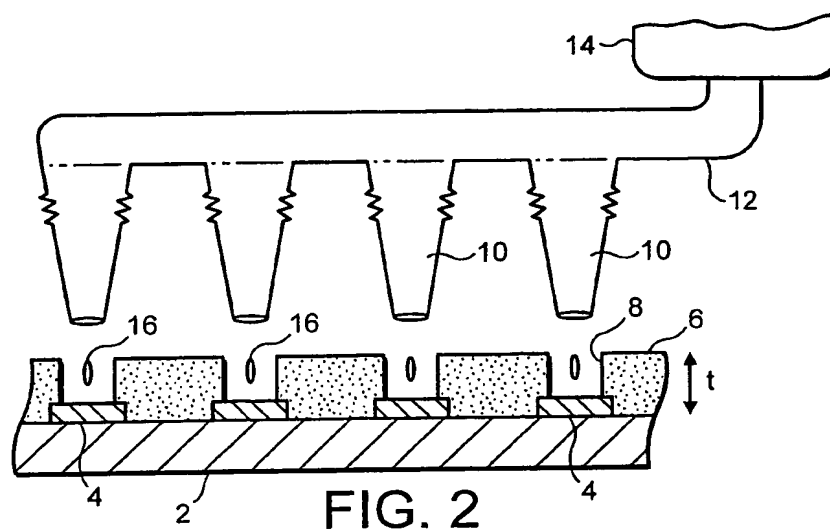


FIG. 2

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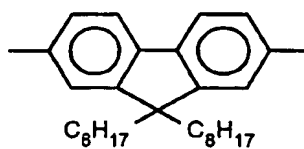


FIG. 3a

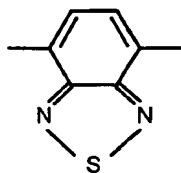


FIG. 3b

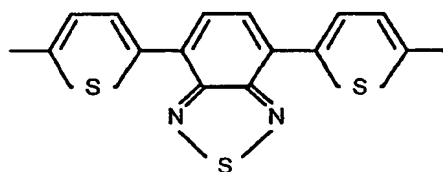


FIG. 3c

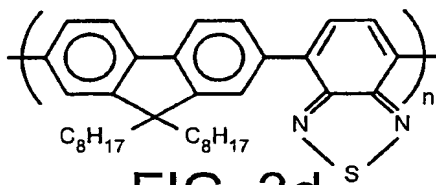


FIG. 3d

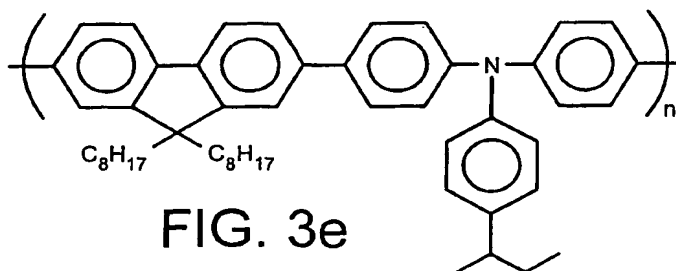


FIG. 3e

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 01/00852

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K11/06 H05B33/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K C08G H01L H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| P,X | JP 2001 052861 A (SHARP CORP., JAPAN) 23 February 2001 (2001-02-23) examples 13,14; table 1 --- | 1-5,10, 11,14-16 |
| X | WO 99 54385 A (DOW CHEMICAL CO) 28 October 1999 (1999-10-28) example 1B --- | 1-5,10, 11 |
| X | US 5 912 473 A (HOTTA SHU ET AL) 15 June 1999 (1999-06-15) example 8 --- | 1-5,10 |
| X | US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) column 7, line 49 - line 50; examples 1,5 --- -/-- | 1-5,10, 11 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | EP 0 825 242 A (SUMITOMO CHEMICAL CO) 25 February 1998 (1998-02-25) page 9, line 22 - line 25 ----- | 1-5, 10 |
| A | WO 99 12398 A (CAMBRIDGE DISPLAY TECH ;FRIEND RICHARD HENRY (GB)) 11 March 1999 (1999-03-11) page 14, paragraph 4 -page 15, paragraph 1 ----- | 10-13 |
| A | WO 99 13692 A (BURROUGHS JEREMY ;GREENHAM NEIL CLEMENT (GB); BRIGHT CHRIS (GB);) 18 March 1999 (1999-03-18) page 29, paragraph 2 ----- | 1-16 |
| A | GB 2 336 553 A (CAMBRIDGE DISPLAY TECH) 27 October 1999 (1999-10-27) cited in the application figure 1 ----- | 14-16 |
| A | EP 0 609 478 A (SPECIALTY COATING SYSTEMS INC) 10 August 1994 (1994-08-10) claim 1 ----- | 14-16 |
| A | EP 0 923 083 A (KEMET ELECTRONICS CORP) 16 June 1999 (1999-06-16) column 2, line 7 - line 9; claims 1,11; example 1 ----- | 1-9 |

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

09/08/2003, EAST Version: 1.04.0000

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 01/00852

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| JP 2001052861 A | 23-02-2001 | NONE | |
| WO 9954385 A | 28-10-1999 | CN 1263542 T EP 0988337 A | 16-08-2000 29-03-2000 |
| US 5912473 A | 15-06-1999 | US 5546889 A US 5556706 A JP 7206599 A | 20-08-1996 17-09-1996 08-08-1995 |
| US 5777070 A | 07-07-1998 | CN 1276806 T EP 1025142 A WO 9920675 A | 13-12-2000 09-08-2000 29-04-1999 |
| EP 0825242 A | 25-02-1998 | JP 10114891 A TW 411728 B US 6207301 B | 06-05-1998 11-11-2000 27-03-2001 |
| WO 9912398 A | 11-03-1999 | NONE | |
| WO 9913692 A | 18-03-1999 | AU 8991598 A EP 1010360 A EP 1062844 A WO 9948337 A | 29-03-1999 21-06-2000 27-12-2000 23-09-1999 |
| GB 2336553 A | 27-10-1999 | DE 19918193 A JP 2000202357 A | 25-11-1999 25-07-2000 |
| EP 0609478 A | 10-08-1994 | CA 2088851 A FI 930518 A JP 6233962 A NO 930407 A US 5266349 A | 06-08-1994 06-08-1994 23-08-1994 08-08-1994 30-11-1993 |
| EP 0923083 A | 16-06-1999 | US 5888582 A CZ 9804036 A JP 11246822 A US 5948234 A | 30-03-1999 15-09-1999 14-09-1999 07-09-1999 |

Form PCT/ISA/210 (patent family annex) (July 1992)

09/08/2003, EAST Version: 1.04.0000